

GLASSCERAMIC MATERIALS

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SINTERED GLASSCERAMIC MATERIALS BASED ON CALCIUM–PHOSPHATE GLASSES

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The particulars of the crystallization of calcium-phosphate glass powders with particle size 90–400 μm are investigated, the structure and phase composition of the crystallized materials are determined, and the sintering regime for narrow powder fractions for obtaining the maximum possible open porosity is optimized. The porosity of the sintered glassceramic materials is 25%, and the pore size is of the order of 100 μm. The materials obtained release into a water medium calcium cations and phosphate anions, which is the price for their successful adaptation in a living organism.

Interest in materials for bone endoprotheses based on calcium phosphates remains unabated, despite the more than 30 year history of the development of such materials. Investigations searching for new solutions which are capable of adapting calcium-phosphate endoprotheses and implants in a living organism and increasing their lifetime and therefore improving the health and extending the active lifetime of people are being conducted intensively in scientific centers in Europe, America, Japan, and China.

The bioactivity of calcium-phosphate materials is due to the presence of calcium and phosphorus oxides in them with molar ratio close to 1.67, characteristic for hydroxyapatite which is the main mineral component of bone. Investigations of calcium phosphates with the ratio of CaO : P₂O₅ from 0.5 to 2.0 have established that practically all of them can bind with bone without encapsulation by connective tissue but the maximum growth rate of bone cells was observed in the presence of hydroxyapatite (1.67) and with whitlockite (1.5). New bone grows more slowly on the surface of materials containing calcium meta- and pyrophosphates [1].

The growth intensity of bone cells also depends on the contact area between the material and the organism's medium. Implants with a developed pore structure with open porosity at least 50% and pore size greater than 100 μm are considered to be most convenient for growth of bone cells and blood vessels.

The nonporous CP glassceramic material with molar ratio CaO : P₂O₅ = 1.1 was synthesized in the system CaO – Al₂O₃ – P₂O₅. The composition of the material is as follows (molar content, %): 39.10 P₂O₅, 43.50 CaO, 4.35 Al₂O₃, 4.35 TiO₂, 4.35 ZrO₂. The founding temperature is 1350°C, the firing temperature is 550°C, and the sintering temperature is 1000°C.

Physical – Chemical Properties of the Materials

Glass density, kg/m ³	2820
CLTE, 10 ^{–7} K ^{–1}	102
Bending strength, MPa:	
glass	50
glassceramic material	100
Microhardness, MPa	4500 ± 87
Chemical resistance	
to distilled water, % losses	0.21 (III hydrolytic class)
Phase composition	α- and β-Ca ₂ P ₂ O ₇ , TiP ₂ O ₇ , ZrP ₂ O ₇

This material has been tested experimentally in animals and has shown good compatibility with soft and bone tissues [2]. Bioactive glass ceramic coating on titanium (RF Patent No. 2157245) and porous granules (RF patent No. 2284158) have been developed based on this material [20]. The coating and the granules are being tested under clinical conditions in the division of otorhinolaryngology at Botkin City Hospital.

The objective of our work is to obtain, on the basis of CP glass, glassceramic materials with developed pore structure

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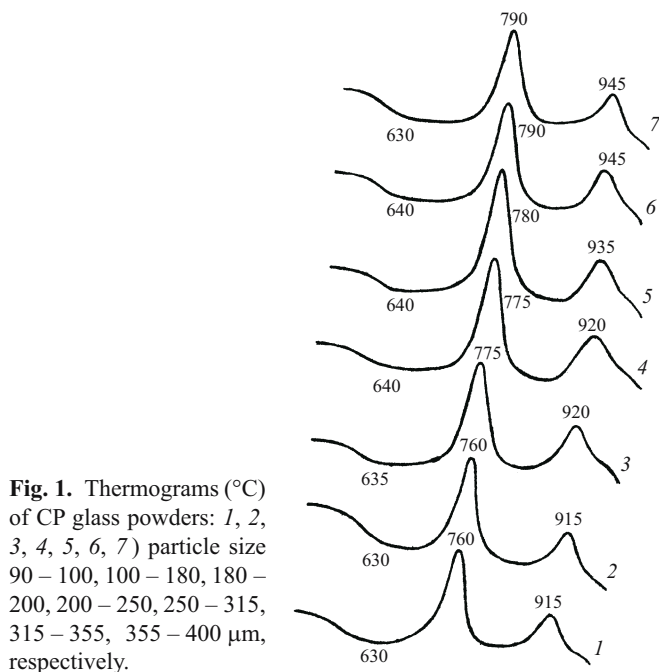


Fig. 1. Thermograms (°C) of CP glass powders: 1, 2, 3, 4, 5, 6, 7) particle size 90 – 100, 100 – 180, 180 – 200, 200 – 250, 250 – 315, 315 – 355, 355 – 400 μm , respectively.

with open porosity and pore size at least 100 μm . It is known that the initial materials for obtaining highly porous structures are highly dispersed powders. In this connection, at the initial stage of these investigations our attention was focused primarily on the effect of the dispersity of the initial glass powders on the temperature-time regime of sintering, the structure, phase composition and physical-chemical properties of the sintered materials.

Powders of CP glass with the following fractional composition (μm) were chosen for the investigations: 90 – 100, 100 – 180, 180 – 200, 200 – 250, 250 – 315, 315 – 355, and 355 – 400. The samples were prepared by semidry pressing using as a temporary binder a 1% solution of polyvinyl alcohol and compaction pressure 2.5 MPa. These samples were loaded into a hot electric furnace, sintering was performed at temperatures 700, 800, 900, 950, and 1000°C with holding time 1 h at each temperature level. The crystallization properties and phase composition of the initial and heat-treated materials were investigated by means of differential-thermal and x-ray phase analysis, the pore size was determined under an optical microscope with 60-fold magnification, and the physical – chemical properties of the sintered materials were determined in accordance with well-known methods and state standards.

The glass powder sinters by the liquid-phase mechanism, and the rate of the process is determined by its viscous properties. For sintering of crystallizing glasses, the parameters of sintering and the characteristics of the sintered glass ceramic materials depend on the crystallization properties of the glass and the flowability of the residual glass phase.

An investigation of the crystallization properties showed that CP glass softens in the temperature range 630 – 640°C, and crystallization occurs in the temperature interval 700 –

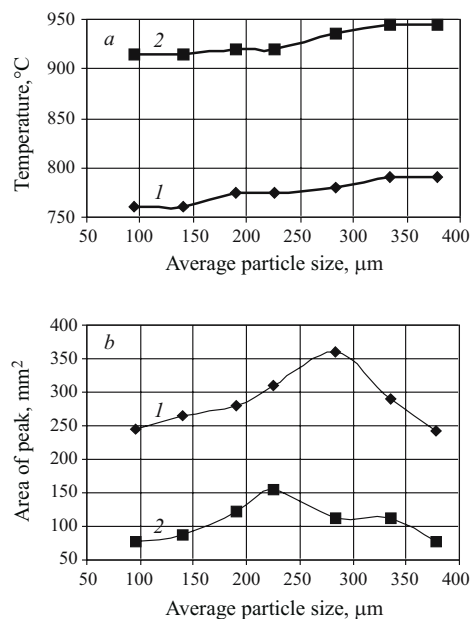


Fig. 2. Effect of the particle size of CP glass powder on temperature (a) and intensity (b) of the crystallization of pyrophosphates: 1, 2) 1st and 2nd exoeffects, respectively.

950°C (Fig. 1). In the process, β -calcium pyrophosphate (exoeffect at 760 – 790°C) and titanium and zirconium pyrophosphates (exoeffect at 915 – 950°C) are formed. As the particles increase in size, the calcium, titanium, and zirconium pyrophosphates crystallize at higher temperatures (Fig. 2). The maximum intensity of calcium pyrophosphate formation is characteristic for powders with average particle size 280 μm , and the average particle size for titanium and zirconium pyrophosphates is 220 μm . Previous investigations [3] have established that the solid solution $\text{Ti}(\text{Zr})\text{P}_2\text{O}_7$ precipitates at 950°C during crystallization of CP glass; this is indicated by the presence of a peak with interplanar distance 3.97 Å in the diffraction patterns.

To determine the temperature range for sintering, the compacts were heat-treated in the range 700 – 1000°C. At 700 and 800°C sintering is incomplete, the materials obtained have low strength and easily crumble under a weak load. Raising the heat-treatment temperature to 900 – 1000°C yields sintered materials, i.e., the flowability of the residual glass phase at temperatures above 800°C gives strong bonding between glass particles even though crystalline phases are formed in them.

CP glass powders sinter in the crystallization temperature range, and calcium, titanium, and zirconium pyrophosphates are identified in the sintered materials; in addition, the particle size affects their formation intensity (Fig. 3). As the sintering temperature of CP glass powder (particle size 250 – 315 μm) increases from 800 to 1000°C, the intensity of the crystallization process for calcium, titanium, and zirconium pyrophosphates increases. The decrease of the crystallization intensity for calcium pyrophosphate at

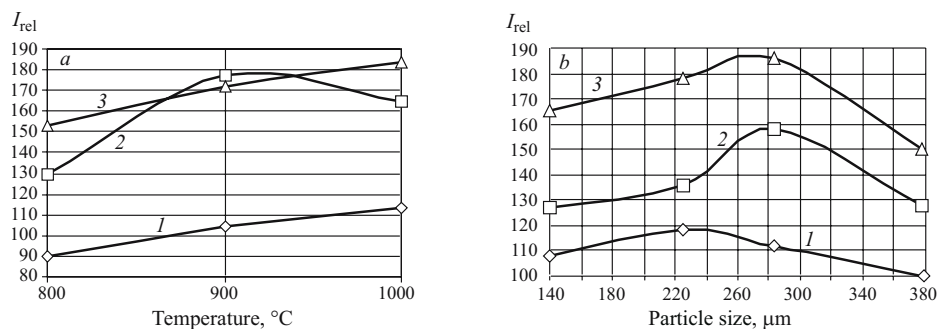


Fig. 3. Effect of temperature (a) and particle size of glass powders (b) on the phase composition of the sintered materials: 1) ZrP_2O_7 ; 2) TiP_2O_7 ; 3) $\text{Ca}_2\text{P}_2\text{O}_7$.

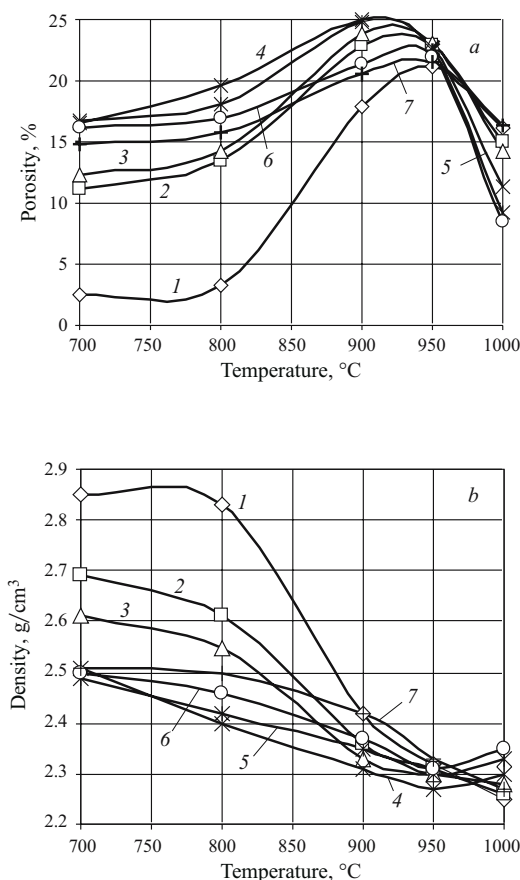


Fig. 4. Effect of heat-treatment temperature on open porosity (a) and apparent density (b) of sintered materials. The labeling is the same as in Fig. 1.

temperatures above 900 $^{\circ}\text{C}$ is due to the onset of melting. The dependences of the relative content of calcium and titanium pyrophosphates on the size of the glass particle sizes for materials sintered at 1000 $^{\circ}\text{C}$ have a maximum corresponding to average particle size 280 μm . Visually, the degree of crystallinity of the materials increases with sintering temperature.

Thus, in materials sintered at temperatures in the range 800 – 1000 $^{\circ}\text{C}$, calcium, titanium, and zirconium pyrophosphates and a residual glass phase are present in different ratios. The sintering and crystallization of CP glass powders occur simultaneously, and the phase composition of the

sintered materials is determined by the particle size of the initial glass powder and by the sintering temperature.

The physical-chemical properties of materials sintered at temperatures in the range 700 – 1000 $^{\circ}\text{C}$ are presented in Fig. 4. It is evident that there is a clear correlation between the open porosity and the apparent density — as temperature increases from 700 to 950 $^{\circ}\text{C}$, the open porosity increases while the apparent density decreases. As the sintering temperature increases to 1000 $^{\circ}\text{C}$, open porosity decreases, which is due to the onset of melting of the calcium pyrophosphates and the residual glass phase, closing of existing pores, and compaction of the sintered materials.

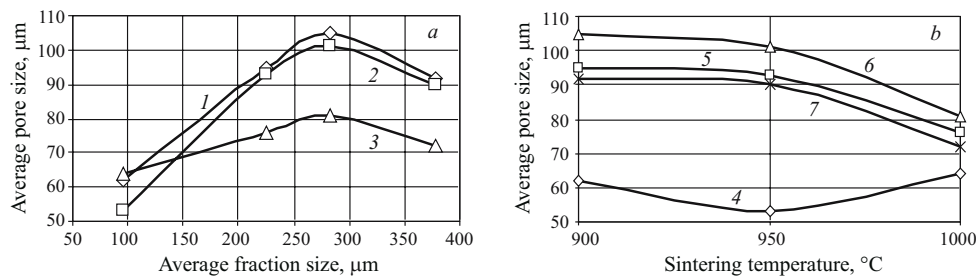
Materials sintered from powders with the central fractions (100 – 180, 180 – 200, 200 – 250, and 250 – 315 μm) at temperatures 900 and 950 $^{\circ}\text{C}$ have the highest open porosity (22 – 24%). At 900 $^{\circ}\text{C}$ the total porosity of these materials is somewhat higher than at 950 $^{\circ}\text{C}$, and at 1000 $^{\circ}\text{C}$ it decreases appreciably to 10 – 15%.

When the small (90 – 100 μm) and large (355 – 400 μm) fractions are sintered, the maximum open porosity 21% is reached at 950 $^{\circ}\text{C}$, and any further decrease of the open porosity with sintering temperature increasing to 1000 $^{\circ}\text{C}$ is not so great (16%). For the 315 – 350 μm fraction, the maximum open porosity 22% is achieved at 950 $^{\circ}\text{C}$, but the decrease of the open porosity with further temperature increases is substantial — to 9%, i.e., practically by a factor of 2.5. The maximum open porosity is characteristic for samples sintered from the middle fractions of glass powders with grain size 200 – 315 μm , and reaches 25% at 900 $^{\circ}\text{C}$.

As the glass particle size increases from 90 to 315 μm , the pore size in the sintered materials increases from 60 to 105 μm while open porosity changes very little. As particle size increases further, the pore size decreases to 90 μm . A gradual decrease of pore size in all sintered materials also occurs as sintering temperature increases from 950 to 1000 $^{\circ}\text{C}$ (Fig. 5).

Thus, sintered materials with open porosity reaching 25% and average pore size of about 95 μm have been obtained in the experimental temperature interval on the basis of CP glass powders with particle sizes ranging from 100 to 450 μm . The nonmonotonic variation of the open porosity of sintered materials with increasing sintering temperature is due to the overgrowth of the pore space as a result of the on-

Fig. 5. Effect of the average glass powder particle size (*a*) and sintering temperature (*b*) on average pore size in sintered materials: 1, 2, 3) sintering temperature 900, 950, and 1000°C, respectively; 4, 5, 6, 7) particle size 90–100, 200–250, 250–315, and 355–400 μm, respectively.



set of melting of crystalline phases at temperatures above 950°C.

In the solubility investigation, the materials sintered from powders with grain sizes 200–250 and 250–315 μm at 950°C with open porosity 25% and average pore size 95 and 100 μm, respectively, were thermostatted in water at 37°C for 1, 7, and 15 days, after which the their mass loss and the pH of the water medium were determined (Fig. 6).

As the thermostating time increases, the mass loss of the sintered materials increases and the pH of the medium decreases somewhat. It is evident that the dependences of the mass loss and the pH on the thermostating are not linear; mass losses increased significantly — by almost a factor of 3 after 15 days of thermostating — and the pH decreased less intensively. This behavior of sintered glass ceramic materials in a water medium is due to the specific nature of the dissolution of materials based on phosphate glasses.

The dissolution of phosphate glasses consists of several repeating stages, in which modifying agents, which are most weakly bound and are mobile (in our case calcium cations), and the glass forming agent (phosphorus oxide), present as phosphate ions in the glass structure (PO_4^{3-} , PO_3^- , and others), participate. After the sintered materials are thermostatted, Ca^{2+} ions and phosphate anions of a different composition, such as, HPO_4^{2-} , H_2PO_4^- , incapable of forming an entire series of compounds in solution which exhibit a weakly acidic reaction, are present in the solution. The cation mobility and the composition of the phosphate anions are determined by the structure and composition of the residual glass phase, and the total solubility of the material consists of the solubility of the glassy and crystalline phases. The solubility of the crystalline calcium, titanium, and zirconium pyrophosphates in water solutions is low, so that in this case the properties of the residual glass phase determine the solubility of the sintered material.

Our investigations have revealed the sintering particulars of calcium-phosphate glass powders with particle sizes 90–400 μm, and they have made it possible to determine the optimal regime and obtain on their basis materials with porosity 20–25% and pore size 80–100 μm, which form a slightly acidic water medium with pH = 6.2–6.4 after 15 days of thermostating in water. The materials obtained release calcium ions and the phosphate anion into the water medium, which is the price for successful adaptation of these materials in the medium inside a living organism.

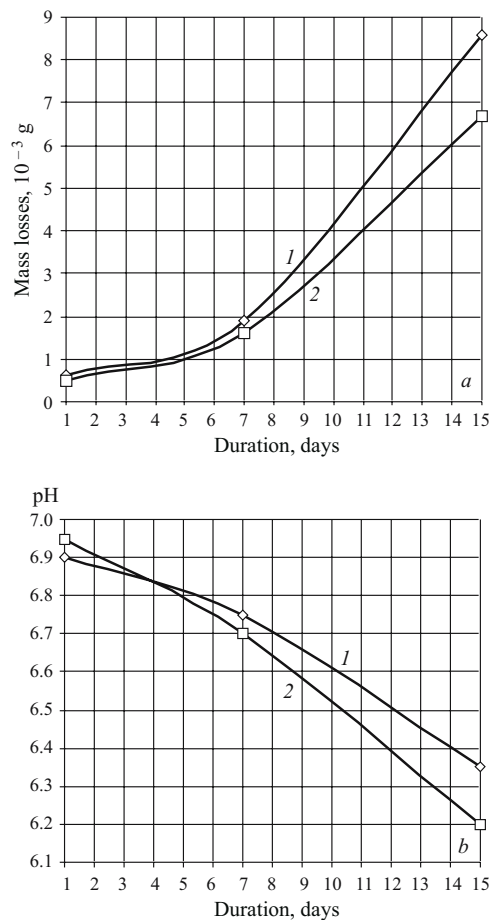


Fig. 6. Effect of the thermostating time and particle size of the initial powders of the sintered materials on the mass loss (*a*) and pH of the medium (*b*): 1, 2) particle size 200–250 and 250–315 μm, respectively.

REFERENCES

1. S. M. Barinov and V. S. Komlev, *Bioceramics Based on Calcium Phosphate* [in Russian], Nauka, Moscow (2005).
2. P. D. Sarkisov, N. Yu. Mikhailenko, and E. E. Stroganova, "Bioactive inorganic materials for bone endoprostheses," *Tekhn. Tekhnolog. Silikatov*, No. 2, 5–9 (1994).
3. E. E. Stroganova and N. Yu. Mikhailenko, "Porous glassceramic granules," in: *Science and Technology of Construction Materials: Status and Prospects for Advancement* [in Russian], Minsk (2005), pp. 16–18.